

Country : Japan
Document No. : 09-194427
Document Type : Kokai
Language : Japanese
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IPC : C 07 C 69/02
B 01 J 23/755
25/02
C 07 C 67/283
//C 07 B 61/00
Application Date : January 18, 1996
Publication Date : July 29, 1997
Foreign Language Title : Howa Esuteru Seizo Hoho
English Title : PRODUCTION PROCESS OF
SATURATED ESTERS

(54) [Title of the Invention]

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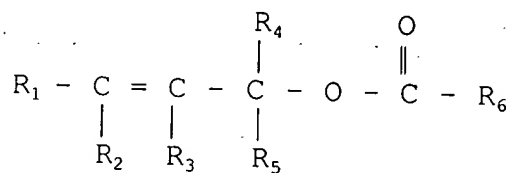
Production Process of Saturated Esters

(57) [Abstract]

[Subject] To provide a process for producing saturated esters by hydrogenation of unsaturated group-containing esters with general-purpose catalysts.

[Solution] A production process of saturated esters, which is characterized by hydrogenation of unsaturated group-containing esters shown by the following general formula (1) with a hydrogenation catalyst containing 10-100 wt% of nickel. The hydrogenation is preferably made at a reaction temperature range of 30-200°C.

[Chem 1]



(Here, R₁, R₂, R₃, R₄, R₅ represent any C₁-C₁₀ alkyl group or hydrogen atom, respectively, and R₆ represents any C₁-C₁₀ alkyl group)

[Claims]

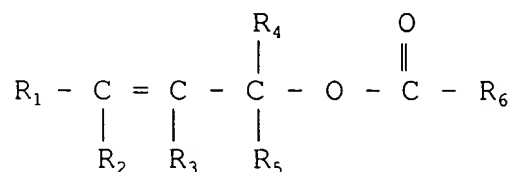
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[Claim 1] A production process of saturated esters, which is

¹Numbers in the margin indicate pagination in the foreign text.

characterized by hydrogenation of unsaturated group-containing esters shown by the following general formula (1) with a hydrogenation catalyst containing 10-100 wt% of nickel.

[Chem 1]



(Here, R_1 , R_2 , R_3 , R_4 , R_5 represent any C_1 - C_{10} alkyl group or hydrogen atom, respectively, and R_6 represents any C_1 - C_{10} alkyl group)

[Claim 2] The production process of saturated esters described in Claim 1, which is characterized by that said unsaturated group-containing esters described in Claim 1 are compounds selected from a group composed of allyl acetate, crotyl acetate, methallyl acetate, allyl propionate, crotyl propionate and methallyl propionate.

[Claim 3] The production process of saturated esters described in Claim 1 or 2, which is characterized by that said hydrogenation catalyst is Raney nickel or a supported nickel.

[Claim 4] The production process of saturated esters described in Claim 1 or 2, which is characterized by hydrogenation in a reaction temperature range of 30-200°C.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] This invention is a production process of saturated esters and relates to a process for producing saturated esters by hydrogenation of unsaturated group-containing esters in the presence of specific catalysts.

[0002]

[Prior Art] Saturated esters are often used as solvents or reaction solvents and are important compounds in the industry. These saturated esters are generally produced through esterification based on the condensation of alcohols and carboxylic acids corresponding to the saturated esters.

[0003]

[Subject to Be Solved by the Invention] In an esterification system, however, if water being a by-product is removed from the system, the equilibrium state of reaction cannot incline to the formation side, thus an industrially significant reactant conversion and reaction rate are not obtained. Therefore, more complicated reactors and reaction engineering through other reaction systems are needed for the industrial production of said saturated esters through the esterification, in addition, such difficulties are present that the space-time yield is low, a lot of energy is also consumed in the distillating separation of water and so on.

[0004] On the other hand, unsaturated group-containing

esters such as allyl, methallyl group and the like can be industrially produced at an extremely high yield and a high space-time yield through oxidative acyloxylation reaction of corresponding olefins and carboxylic acids. Therefore, when the production of saturated esters is attempted by carrying out the hydrogenation with these easily available unsaturated group-containing esters, this reaction was also accompanied by a decomposition reaction of said saturated esters into an alkane and a carboxylic acid. To prevent the decomposition and obtain the saturated esters in a high yield, it becomes necessary to use rhodium (Rh) being a platinum metal as catalyst (*Catalytic hydrogenation*; Shigeo Nishimura, Tokyo Kagaku Dojin, pl17). However, Rh is an extremely expensive metal even in the platinum metals. If it is considered that relatively cheap compounds like saturated esters are industrially produced with Rh as catalyst and the deactivation of catalyst is unavoidable to some extent, this causes an unbalance in economy.

[0005]

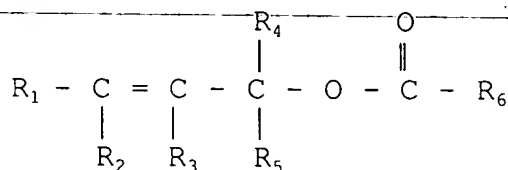
[Means for Solving the Subject] The inventors repeated earnest studies on the hydrogenation of unsaturated group-containing esters, consequently they unexpectedly discovered that saturated esters are obtained in a high yield with almost no decomposition reaction, thus came to accomplish this invention.

[0006] Namely, this invention is a production process of

saturated esters which is characterized by hydrogenation of unsaturated group-containing esters shown by the following general formula (1) with a hydrogenation catalyst containing 10-100 wt% of nickel. Moreover, this invention is to provide said production process of saturated esters which is characterized by that said unsaturated group-containing esters described in Claim 1-are compounds selected from a group composed of allyl acetate, crotyl acetate, methallyl acetate, allyl propionate, crotyl propionate and methallyl propionate. Furthermore, this invention is to provide said production process of saturated esters which is characterized by that said hydrogenation catalyst is Raney nickel or a supported nickel. Besides, this invention is to provide said production process of saturated esters which is characterized by hydrogenation in a reaction temperature range of 30-200°C. This invention is described in detail below.

[0007]

[Chem 2]



(Here, R_1 , R_2 , R_3 , R_4 , R_5 represent any C_1 - C_{10} alkyl group or hydrogen atom, respectively, and R_6 represents any C_1 - C_{10} alkyl group)

[0008]

[Embodiment of the Invention] In this invention, the unsaturated group-containing esters shown by the above general formula (1) can be used as materials of said saturated esters. Here, R_1 , R_2 , R_3 , R_4 , R_5 represent any C_1 - C_{10} alkyl group or hydrogen atom and may be same or different, respectively, and the alkyl groups may be straight-chain or branched. R_6 is any C_1 - C_{10} alkyl group and may be straight-chain or branched. Most preferable ones usable in this invention are allyl ester in which all the R_1 , R_2 , R_3 , R_4 , R_5 are hydrogen atoms, crotyl esters in which R_3 is methyl and all the R_1 , R_2 , R_4 , R_5 are hydrogen atoms, and methallyl esters in which R_1 is methyl and all the R_2 , R_3 , R_4 , R_5 are hydrogen atoms. More specifically, they are allyl acetate, allyl propionate, methallyl propionate, methallyl acetate, crotyl propionate, crotyl acetate and the like can be preferably used, more preferably are allyl acetate, crotyl acetate and methallyl acetate.

[0009]

The catalysts used in this invention are hydrogenation catalysts with nickel as main component, catalysts containing 10-100 wt% nickel are preferable, and catalysts containing 20-90 wt% nickel are preferable. For the form of catalysts, nickel may be contained as alloys or may be supported on carriers. More specifically, nickel alloys such as Raney nickel and the like,

supported nickel catalysts supported on a carrier such as kieselguhr and the like, Urushihara Nickel catalyst being a nickel compound and so on can be exemplified. Moreover, commercial products are easily available on an industrial scale. Furthermore, besides nickel, a very small amount of other ingredients, e.g., Cu, Cr, Mg, Al and so on sometimes is added to commercial nickel catalysts for improvements of activity, poisoning resistance, heat resistance and acid resistance of said catalysts, such catalysts can also be preferably used in this invention.

[0010]

Either gas phase process or liquid phase process is possibly used as reaction forms in this invention. In the case of gas phase reaction, the use of a fixed bed flow reactor is the commonest, but the use of a fluidized bed reactor is also possible. In the case of liquid phase reaction, it can be carried out in the form of a complete mixed tank, bubble tower, trickle bed and the like.

[0011]

The reaction temperature also varies with the kind of materials, but it is preferably in a range of 30-200°C, and more preferably in a range of 50-150°C. A sufficient reaction rate is not obtained if the reaction temperature is below 30°C and the hydrogenolysis proceeds if it is above 200°C, thus the both are

undesirable. It is preferable that The reaction temperature is preferably in a temperature range of 50-150°C when ally acetate is used as material.

[0012]

A sufficient activity is usually obtained even if the reaction pressure is normal pressure in the case of gas phase reaction. Therefore, it is highly convenient to carry out the reaction at normal pressure. However, the reaction can be further accelerated by taking pressure conditions. In this case, it is sufficient that the pressure condition is 10 kg/cm² or below. On the other hand, in the case of liquid phase reaction, a pressure usually becomes necessary to ensure the concentration of dissolved hydrogen. The reaction pressure in this case is preferably in a range of 10-100 kg/cm², and more preferably 15-50 kg/cm². The reaction is not fully accelerated if the pressure is below 10 kg/cm², while the hydrogenolysis becomes predominant if it is above 100 kg/cm², thus the both are undesirable.

[0013]

Saturated esters such as n-propyl acetate, butyl acetate, isopropyl acetate, n-propyl propionate, butyl propionate, isopropyl propionate and the like can be obtained by this invention.

[0014]

[Actual Examples] This invention is specifically illustrated

by actual examples and comparison examples below, but this invention is not restricted to these examples. Moreover, definitions of conversion, selectivity and yield in the actual examples are based on the following formulas.

[0015]

[Math 1]

$$\begin{aligned} \text{Conversion (\%)} &= \frac{\text{Mole number of unsaturated group-} \\ &\quad \text{containing ester consumed in reaction}}{\text{Mole number of unsaturated group-} \\ &\quad \text{containing ester charged in reactor}} \times 100 \\ \text{Selectivity (\%)} &= \frac{\text{Mole number of formed saturated ester}}{\text{Mole number of unsaturated group-} \\ &\quad \text{containing ester consumed in reaction}} \times 100 \\ \text{Yield (\%)} &= \frac{\text{Mole number of formed saturated ester}}{\text{Mole number of unsaturated group-} \\ &\quad \text{containing ester charged in reactor}} \times 100 \end{aligned}$$

[0016]

[Actual Example 1] 6 mL of a supported nickel catalyst ("N111" made by Nikki Chemical Ltd., nickel content 46 wt%, cylin-drical moldings) was packed in a stainless steel U-shaped reaction tube of 18 mmφ in inner diameter. The catalyst was pretreated at 170°C (the maximum value in the catalyst layer, same hereafter) for 6 hr while a hydrogen gas flowed at normal temperature and 5.6 L/hr (STP value, same hereafter). Subsequently, the reaction is conti-nued at 150°C for 6 hr while 5.2 g/hr of allyl acetate and 5.6 L/hr of hydrogen gas were

charged. The condensate at the exit of reactor was analyzed by gas chromatography, as a result, the conversion of allyl acetate was 96.5%, the selectivity of n-propyl acetate 96.2%, and the yield of n-propyl acetate 92.8%.

[0017]

[Actual Example 2] The reaction was carried out in all the same way as Actual Example 1 except that the reaction temperature was changed to 100°C. The conversion of allyl acetate was 96.5%, the selectivity of n-propyl acetate 99.1%, and the yield of n-propyl acetate 95.6%.

[0018]

[Actual Example 3] The reaction was carried out in all the same way as Actual Example 1 except that the reaction temperature was changed to 230°C. The conversion of allyl acetate was 98.7%, the selectivity of n-propyl acetate 66.7%, and the yield of n-propyl acetate 65.8%.

[0019]

[Actual Example 4] 200 mL of allyl acetate and 10 g of Raney nickel (treated for alkali development : "N154" made by Nikki Chemical Ltd., nickel content 50 wt% before the development) were charged in a 1000 mL stainless steel autoclave and reacted for 2 hr while stirring at hydrogen pressure of 30 kg/cm² (gage pressure) and reaction temperature of 100°C. The reaction solution was analyzed by gas chromatography, as a

result, the conversion of allyl acetate was 97.3%, the selectivity of n-propyl acetate 93.6%, and the yield of n-propyl acetate 91.1%.

[0020]

[Effects of the Invention] This invention enables to produce saturated esters in the industry while maintaining high reactant conversion, selectivity and yield. Moreover, a complicated reactor and reaction engineering were not needed. The reaction catalyst used by this invention enables to make it easy available and cheaply produce saturated esters in the industry because the catalyst differs from commonly used rhodium in the platinum metals and takes cheap nickel as main component.